University of Groningen

Thienyl analog of 1-(3-methoxycarbonyl)propyl-1-phenyl-[6,6]-methanofullerene for bulk heterojunction photovoltaic devices in combination with polythiophenes

Popescu, Lacramioara M.; van 't Hof, Patrick ; Sieval, Alexander B.; Jonkman, Harry T.; Hummelen, Jan C.

Published in:
Applied Physics Letters

DOI:
10.1063/1.2397003

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2006

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):
Popescu, L. M., van 't Hof, P., Sieval, A. B., Jonkman, H. T., & Hummelen, J. C. (2006). Thienyl analog of 1-(3-methoxycarbonyl)propyl-1-phenyl-[6,6]-methanofullerene for bulk heterojunction photovoltaic devices in combination with polythiophenes. *Applied Physics Letters*, *89*(21), 213507-1 - 213507-3. [213507]. https://doi.org/10.1063/1.2397003

Copyright
Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment.

Take-down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): http://www.rug.nl/research/portal. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

Thienyl analog of 1-(3-methoxycarbonyl)propyl-1-phenyl-[6,6]-methanofullerene for bulk heterojunction photovoltaic devices in combination with polythiophenes

Lacramioara M. Popescu, Patrick van 't Hof, Alexander B. Sieval, Harry T. Jonkman,[a] and Jan C. Hummelen
Molecular Electronics, Materials Science Centre, University of Groningen, Nijenborgh 4, NL-9747 AG Groningen, The Netherlands

(Received 17 August 2006; accepted 17 October 2006; published online 20 November 2006)

An analog of 1-(3-methoxycarbonyl)propyl-1-phenyl-[6,6]-methanofullerene (PCBM) was designed with the aim of improving miscibility with polythiophene donors, especially poly(3-hexyl thiophene) (P3HT). In the title compound the phenyl group from PCBM is replaced by a thienyl group, it is named 1-(3-methoxycarbonyl)propyl-1-thienyl-[6,6]-methanofullerene (ThCBM). In this letter, experimental studies of the morphology, charge transport, and solar cell performance in blends of P3HT:ThCBM are reported. This may open a route for the design of more specific fullerene based acceptor materials, which may optimize the morphology of bulk heterojunction photovoltaic devices with respect to their transport. © *2006 American Institute of Physics*.
[DOI: 10.1063/1.2397003]

Organic photovoltaic devices consisting of three dimensional interpenetrating networks of conjugated polymers and a C_{60} derivative represent a challenging alternative for renewable sources of electrical energy.[1] In the last few years, several efforts to improve the efficiencies of these devices were undertaken.[2–4] One major improvement to this device structure was obtained by optimizing the morphology of the blend by casting the polymer and 1-(3-methoxycarbonyl) propyl-1-phenyl-[6,6]-methanofullerene (PCBM) from a solvent that prevents large scale phase separation and enhances the polymer chain packing. Bulk heterojunction solar cells made from poly[2-methoxy-5-(3′, 7′-dimethyloctyloxy)-1, 4-phenylene vinylene] (MDMO-PPV) and PCBM reached a power conversion efficiency of 2.5%.[2] A step forward towards higher efficiency was reached by replacing MDMO-PPV with a high-mobility polymer as the light absorber and the electron donating material. For pristine regioregular poly(3-hexyltheopene) (P3HT), the highest reported hole mobility amounts to 0.1 $cm^2\ V^{-1}\ s^{-1}$,[5] whereas the hole mobility of pristine MDMO-PPV measured under the same circumstances is $5\times10^{-4}\ cm^2\ V^{-1}\ s^{-1}$.[6] Moreover, P3HT has the advantage of an enhanced photostability and an improved optical absorption in the visible region which results in a better overlap with the solar emission compared to MDMO-PPV. The most promising polymer solar cells developed to date in terms of efficiency and stability is based on a combination of P3HT as donor and PCBM as acceptor.[7] The efficiency of solar cells based on P3HT and PCBM was shown to depend strongly on the processing conditions, and, in particular, it shows an improvement when the devices are thermal annealed.[7]

A replacement of PCBM in bulk heterojunction photovoltaic devices was not found so far. Herein, an analog of PCBM was designed with the aim of improving miscibility with polythiophene donors, especially P3HT. In this compound the phenyl group from PCBM is replaced by a thienyl group, resulting in 1-(3-methoxycarbonyl) propyl-1-thienyl-[6,6]-methanofullerene (ThCBM) (see inset of Fig. 1). Subtle as this modification may seem, we have previously observed that even slight modifications of the PCBM structure may lead to significant changes in its solubility, the morphology of the spin coated films, and charge carrier transport. The synthesis of this compound was done using procedures as described for PCBM (Ref. 8) (see supporting information). Cyclic voltammetry measurements of ThCBM show that the energy levels of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are identical to those of PCBM. In this letter we report experimental studies of the morphology, charge transport, and solar cell performance in blends of P3HT:ThCBM. The results indicate that ThCBM provides the same charge carrier mobility as PCBM and that a highly functional bulk heterojunction morphology with P3HT can be obtained.

Prior to investigating solar cells made with this methanofullerene as active layer component, it is important to determine its electron transport properties, since this is a relevant parameter which strongly influences the solar cell performance.[9] For films of pristine PCBM, spin coated from

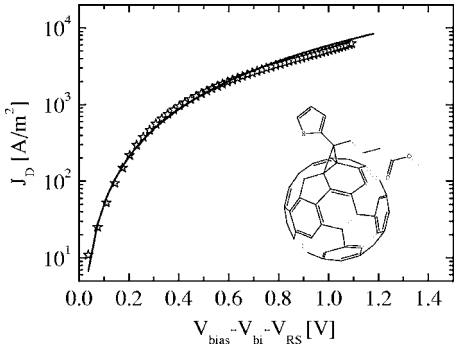

FIG. 1. Experimental (symbols) and calculated (solid line) J_D-V characteristics for ITO/PEDOT:PSS/ThCBM/LiF/Al electron-only device with a thickness $L=102$ nm. J_D is plotted against the applied voltage (V_{bias}), corrected for the built-in voltage (V_{bi}) and the voltage drop over the ITO/PEDOT:PSS layers (V_{RS}, RS=18 Ω). The inset shows the molecular structure of ThCBM.

[a]Electronic mail: harry.jonkman@rug.nl

 © 2006 American Institute of Physics
Downloaded 18 Dec 2006 to 129.125.25.39. Redistribution subject to AIP license or copyright, see http://apl.aip.org/apl/copyright.jsp

a chlorobenzene solution, an electron mobility of 2×10^{-3} cm^2 V^{-1} s^{-1} has been observed.[10] ThCBM is not as soluble as PCBM in chlorobenzene but it dissolves readily in *ortho*-dichlorobenzene (ODCB). Hence, for a better comparison, the electron mobilities of PCBM and ThCBM were determined in films spun from ODCB solution.

The devices were prepared on indium tin oxide (ITO) covered glass substrates, which were cleaned using normal cleaning procedure and finalized by exposing in a vacuum plasma cleaner for 20 min. Subsequently, a 60 nm thick layer of poly(3,4-ethylenedioxythiophene:poly(styrenesulfonate) (PEDOT:PSS) was spin coated from an aqueous dispersion under ambient conditions. Afterwards the layer was dried in the laboratory oven at 140 °C for 10 min. A thin layer (≈200 nm) of a blend of P3HT:ThCBM (50:50 wt %) solution in chloroform was spin coated on top of a PEDOT:PSS layer using a Karl Suss spin coater. To complete the solar cell devices, Sm (5 nm), and subsequently Al (100 nm) electrodes were deposited by thermal evaporation under vacuum (1×10^{-7} mbar). The thermal annealing was performed on complete P3HT:ThCBM devices in the nitrogen (N_2) atmosphere on a hot plate at 150 °C for 4 min. The electron-only and the hole-only devices used to investigate the electron transport in the pristine ThCBM (and PCBM) films and the hole transport in P3HT:ThCBM films were fabricated in the same way as was presented above except for the top electrode which was replaced with a lithium fluoride (LiF, 1 nm)/Al (100 nm) electrode for electron-only devices, and Pd (50–60 nm) in the case of hole-only devices. Current density–voltage (*J-V*) characteristics were measured at room temperature, inside the N_2 glove box, with a computer-controlled Keithley 2400 source meter, in the dark or under illumination by a halogen lamp. The morphology of the representative films was determined using atomic force microscopy (AFM) operating in a tapping mode with a silicon cantilever, under ambient conditions.

Among the various methods to determine the charge carrier mobility we regard the most appropriate one, the analysis of the space-charge limited current (SCLC) by investigating its (*J-V*) characteristics in the dark. For a trap-free semiconductor, assuming that the injecting contact is Ohmic, the SCLC is given by the Mott-Gurney[11] equation $J \propto \mu V^2 L^{-3}$, where μ is the charge carrier mobility, V is the applied voltage, and L is the thickness of the active layer. The dependence of the charge carrier mobility on the electric field must be taken into account for disordered organic materials. Thus, the SCLC is given by[12]

$$J_D = \frac{9}{8}\epsilon_0 \epsilon_r \mu_e \exp\left(0.89\gamma\sqrt{\frac{V}{L}}\right)\frac{V^2}{L^{-3}}, \quad (1)$$

where μ_e is the zero-field electron mobility, ϵ_0 is the vacuum permittivity, ϵ_r is the relative dielectric constant, γ the field activation factor, and V/L is the applied electric field (E). The ϵ_r for ThCBM as well as for PCBM (≈3.9) was determined from impedance spectroscopy measurements. Hence, the only unknown parameter in Eq. (1) is the charge carrier mobility. The J_D-V characteristics of an electron-only pristine ThCBM device, measured at room temperature, are depicted in Fig. 1. The active area was 0.1 cm^2. Based on the work function of ITO/PEDOT:PSS (≈5.2 eV) and LiF/Al (≤3.7 eV), compared with the HOMO (6.1 eV) and LUMO (3.7 eV) levels of ThCBM, one can assume that the current through the device is dominated by the electrons, since only electrons are injected from LiF/Al electrode in the forward bias (when ITO is positively biased). The value of μ_e was extracted by fitting Eq. (1) to the experimental data, as shown in Fig. 1. Thus ThCBM showed a μ_e of $1.8(\pm 0.8) \times 10^{-3}$ cm^2 V^{-1} s^{-1} at room temperature. For PCBM films, spin coated from ODCB solution, a μ_e of $1.4(\pm 0.5) \times 10^{-3}$ cm^2 V^{-1} s^{-1} was obtained accordingly. These values of μ_e are similar to those observed previously for PCBM films spun from chlorobenzene.[10] Moreover, both methanofullerenes have the same electron mobility, which indicates that the electron transport properties of PCBM are not altered upon replacing the phenyl group by a thienyl moiety.

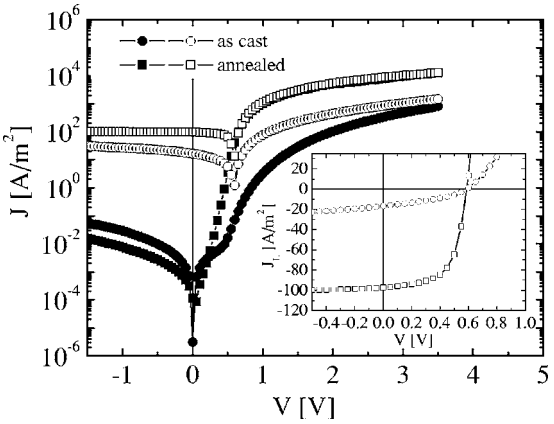

FIG. 2. *J-V* characteristics of ITO/PEDOT:PSS/P3HT:ThCBM/Sm/Al devices as cast (circles) and after thermal annealing (squares) are shown in a semilogarithmic plot. The devices were measured at room temperature (295 K) in the dark (full symbols) and under illumination (empty symbols) through the transparent ITO electrode. The devices under illumination were measured by a halogen lamp with intensity of 100 mW/cm^2, calibrated using a reference silicon diode. The inset shows the *J-V* characteristics under illumination in a linear scale.

In the following we studied the influence of the thermal annealing of a photoactive P3HT:ThCBM layer on the solar cell performance. The P3HT:ThCBM blend devices are made as was described above. The *J-V* characteristics of the solar cell devices, in the dark and under illumination, as cast and after thermal annealing are represented in Fig. 2. A substantial increase in the current is observed upon annealing, reflecting a higher overall mobility. For the as cast devices the performance characteristics were short circuit current density (J_{SC})=14.35 A/m^2, open circuit voltage (V_{OC})=0.59 V, fill factor (FF)=36.5%, and power conversion efficiency (η)=0.31%. After thermal annealing the J_{SC} increased to 83.65 A/m^2. Due to annealing, the overall polymer crystallinity has improved and the hole mobility is increased, as will be demonstrated in the following. The devices show an increase in FF from 36.6% to 61.4% upon thermal annealing. This suggests an increase in carrier transport and it results in η of 3.03%.

In order to investigate the hole transport through the P3HT phase in a blend with ThCBM, the electron current through the ThCBM phase has to be blocked. This can be done by choosing proper electrodes which suppress the injection of electrons into the device, resulting in a hole-only device. Herein the hole-only devices were fabricated with the following structure: ITO/PEDOT:PSS/P3HT:ThCBM/Pd. The work function of PEDOT:PSS is about 5.2 eV. Hence, PEDOT:PSS serves as an Ohmic contact for hole injection

Downloaded 18 Dec 2006 to 129.125.25.39. Redistribution subject to AIP license or copyright, see http://apl.aip.org/apl/copyright.jsp

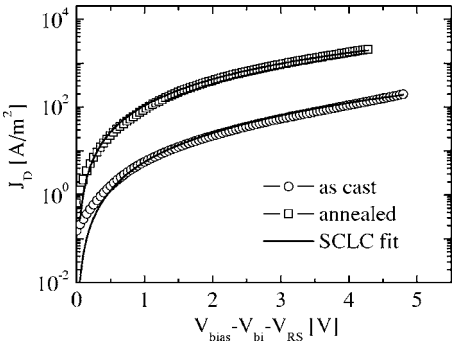

FIG. 3. Experimental (symbols) and calculated (solid lines) J_D-V for an ITO/PEDOT:PSS/P3HT:ThCBM/Pd hole-only device, as cast and after thermal annealing (see legend). The active layer thickness is $L=145$ nm.

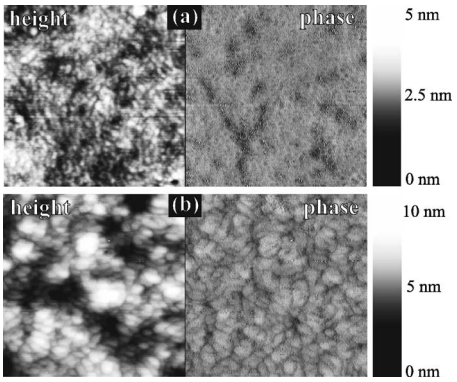

FIG. 4. 500×500 nm^2 AFM height and simultaneously taken phase images of P3HT:ThCBM films, as cast (a) and after thermal annealing (b).

into HOMO of P3HT [≈4.9 eV (Ref. 13)]. The work function of Pd is about 5.12 eV, which leads to a large mismatch with the LUMO of ThCBM (Ref. 14) and this prevents injection of the electrons into ThCBM. When the applied voltage exceeds built-in voltage (V_{bi}) in this hole-only device, the transport of holes through the P3HT is limited by the space charge that accumulates, and consequently the current is described by Eq. (1). The experimental J_D of P3HT:ThCBM blends that were measured in hole-only device configuration, as cast and after thermal annealing, are shown in Fig. 3. Assuming that the device is hole dominated, the J_D-V measurements then provide information on the zero-field hole mobility (μ_h) of the P3HT phase in a blend. For as cast films, the μ_h in blend of P3HT:ThCBM (50:50 wt %) is approximately 2×10^{-6} cm^2 V^{-1} s^{-1} and the field activation factor γ is 1.5×10^{-4} m$^{0.5}$ V$^{-0.5}$. Upon thermal annealing of P3HT:ThCBM films an enhancement of the hole mobility by a factor of 100 was observed ($\mu_h\approx2\times10^{-4}$ cm^2 V^{-1} s^{-1}).

The AFM images of the P3HT:ThCBM films for as cast and after thermal annealing are shown in Fig. 4. It has been shown that whisker morphology is present in P3HT.[15] In pristine P3HT, this predominantly polycrystalline film may be formed already during the coating process and the thermal annealing does not further improve the crystallinity. A phase image of a P3HT:ThCBM spin coated film as cast [see Fig. 4(a)] reveals an amorphous structure. In a blend film the presence of another molecule, in this case ThCBM, might prevent crystallization of P3HT. Upon thermal annealing, more structures can be seen in the spin coated film under the AFM [see Fig. 4(b)], demixing of the two components is increased, and the crystallinity of the P3HT is enhanced.[16] At this point the researcher is tempted to believe that the resulting interpenetrating network provides continues pathways in the entire photoactive layer for efficient charge carrier transport.

In conclusion, we have investigated the ThCBM for application as an acceptor material in bulk heterojunction solar cells. The electrical characterization of pristine ThCBM films reveals that its electron transport properties equal those of PCBM, which indicates that the electron transport properties are not altered upon replacing the phenyl group by a thienyl moiety. Using ThCBM in combination with P3HT as the donor counterpart the improved morphology after thermal annealing and the optimized absorber composition leads to a power conversion efficiency of 3.0%. The increase of efficiencies is due to the increasing crystallinity of P3HT and hence the enhancement of the hole mobility in the P3HT phase of the blend by two orders of magnitude relative to as cast devices.

The authors are indebted to Bert de Boer for the purification of the regioregular P3HT polymer.

[1] *Organic Photovoltaics: Concepts and Realizations*, edited by C. J. Brabec, V. Dyakonov, J. Parisi, and N. S. Sariciftci (Springer, Heidelberg, 2003), Vol. 60, p. 152.
[2] S. E. Shaheen, C. J. Brabec, N. S. Sariciftci, F. Padinger, T. Fromherz, and J. C. Hummelen, Appl. Phys. Lett. **78**, 841 (2001).
[3] N. S. Sariciftici, L. Smilowitz, A. J. Heeger, and F. Wudl, Science **258**, 1474 (1992).
[4] G. Yu, J. Gao, J. C. Hummelen, F. Wudl, and A. J. Heeger, Science **270**, 1789 (1995).
[5] H. Sirringhaus, N. Tessler, and R. H. Friend, Science **280**, 1741 (1998).
[6] M. C. J. M. Vissenberg and M. Matters, Phys. Rev. B **57**, 12964 (1998).
[7] F. Padinger, R. S. Rittberger, and N. S. Sariciftci, Adv. Funct. Mater. **13**, 85 (2003).
[8] J. C. Hummelen, B. W. Knight, F. LePeg, F. Wuddl, J. Yao, and C. L. Wilkins, J. Org. Chem. **60**, 532 (1995).
[9] V. D. Mihailetchi, L. J. A. Koster, P. W. M. Blom, C. Melzer, B. de Boer, J. K. J. van Duren, and R. A. J. Janssen, Adv. Funct. Mater. **15**, 795 (2005).
[10] V. D. Mihailetchi, J. K. J. van Duren, P. W. M. Blom, J. C. Hummelen, R. A. J. Janssen, J. M. Kroon, M. T. Rispens, W. J. H. Verhees, and M. M. Wienk, Adv. Funct. Mater. **13**, 43 (2003).
[11] K. C. Kao and W. Hwang, *Electrical Transport in Solids* (Pergamon, Oxford, 1981), Vol. 14, p. 151.
[12] P. N. Murgatroyd, J. Phys. D **3**, 151 (1970).
[13] Y. Kim, S. A. Choulis, J. Nelson, D. D. Bradley, S. Cook, and J. R. Durrant, Appl. Phys. Lett. **86**, 063502 (2005).
[14] V. D. Mihailetchi, P. W. M. Blom, J. C. Hummelen, and M. T. Rispens, J. Appl. Phys. **94**, 6849 (2003).
[15] J. K. Ihn, J. Moulton, and P. Smith, J. Polym. Sci., Part B: Polym. Phys. **31**, 735 (1993).
[16] X. Yang, J. Loos, S. C. Veenstra, W. J. H. Verhees, M. M. Wienk, J. M. Kroon, M. A. J. Michels, and R. A. J. Janssen, Nano Lett. **5**, 579 (2005).

Downloaded 18 Dec 2006 to 129.125.25.39. Redistribution subject to AIP license or copyright, see http://apl.aip.org/apl/copyright.jsp